

*Some Observations of the Electrical action of Light upon Silver and its Haloid Compounds:—By Colonel J. WATERHOUSE, I. S. C., Assistant Surveyor General of India.*

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In my paper on "Electro-chemical Reversals with Thio-carbamides," read at the meeting of the Society in April 1891, it was shown that the peculiar reversals of the photographic image produced by the addition of very minute quantities of a thio-carbamide, or sulpho-urea, to an eikonogen developer appeared to be connected with and accompanied by electro-chemical action, if not actually brought about by it. It was remarked also that the experiments brought forward pointed to the conclusion that, at any rate as regards the haloid salts of silver, the formation and development of the photographic image is to a very great extent influenced by electrical action, more so perhaps, than has generally been recognised, although the fact of photographic action being accompanied by electrical phenomena has been known since the earliest days of photography. It was suggested that a further investigation into the theory of photography based on electro-chemical laws, might be of value in throwing light upon much that is now obscure and uncertain as regards the formation and development of the invisible photographic image formed by the exposure to light of silver haloid compounds.

Since that time I have given a good deal of attention to the subject and tried several experiments in various ways with the object of ascertaining the electrical action of light, in connection with photography, on plates of pure silver immersed in various fluids as well as on dry plates and other forms of silver haloid compounds in ordinary photographic use. Also on the action of electrical currents in forming developable compounds of silver haloids similar to those formed by light, and, further, on the electrolysis of ordinary photographic developers and on the currents produced during the development of the photographic image. These observations are not yet sufficiently complete to found any sound deductions upon, but I hope to complete them later. In the meantime, I have thought that a short note on some observations I have lately made on the electrical action of light upon plain silver plates in various solutions, might be of interest and form a suitable introduction to any further notes on this subject I may be able to bring before you. It does not pretend to be complete or exhaustive, and can only be considered as a contribution towards a systematic investigation of the question.

A great many observations have been made from time to time of the electrical influence of light on metals immersed in water and various saline solutions, and before going further, it seems desirable to give a brief summary of these observations, and more particularly of those relating to silver and its salts.

More than half a century ago, in 1839, Edmond Becquerel was the first to show that the electrical action accompanying the chemical changes brought about by the influence of light upon various substances, including several metals and the silver haloids, could be observed with the aid of a very delicate galvanometer. He found that this action was quite independent of any calorific radiation or heating of one electrode more than another, but was powerfully affected by the different rays of the spectrum, the greatest action being produced by the violet, indigo and blue rays, while with the green, yellow and red rays there was little or no action. Becquerel's observations are fully summarized in his work, "*La Lumière, ses causes et ses effets*," Vol. II. To observe these effects he used a covered vessel divided into two parts by a thin membrane. In each of the compartments he placed a plate of platinum or gold, previously made red-hot to remove all impurities, the plates being connected with the poles of a very sensitive galvanometer, and laid horizontally in the apparatus. Each compartment had a moveable cover. He found that when the two compartments contained an alkaline solution, the plate exposed to the solar rays took negative electricity, while the reverse occurred if the solution were acid. With alterable metals, such as silver or brass, analogous effects were obtained and the electrical effect could be largely increased by giving the plates a preliminary polarisation by plunging them in water and then placing them in connection with the positive pole of a battery. When two silver plates were immersed in water acidulated with nitric acid exposure to light of one plate only produced a very weak current and the exposed plate was always positive. If the gold or platinum plates had been thoroughly cleaned, had remained in strong nitric acid and had been made red hot, the different parts of the spectrum were almost powerless to produce electric currents. With well cleaned silver plates which had been heated several times the effects were also almost *nil*, though not quite absent, and from this fact it seemed possible that when the plates were not in this state the effects produced might be due to the action of light upon corpuscles of organic matter adhering to the plates which become oxidised by the action of light, the water supplying the oxygen. If this effect did not take place and there was no alteration in the plates themselves the light must produce a disturbance of the particles, but the former supposition seemed most probable. He found that when

silver chloride, iodide or bromide, precipitated in a thin layer on sheets of platinum or gold, was exposed to light as above, the exposed plate was positive, and that the initial action was much stronger with the bromide than with the chloride; though the intensity of the currents observed was variable and depended on the thickness of the film of bromide, moreover the electrical action was soon exhausted. With the iodide the current was almost as strong as with the chloride, but did not remain constant so long.

When plates of silver were employed, instead of platinum or gold, as a support for the haloids, the effects noted were stronger and more regular, but it was found that the direction of the current depended on the thickness of the films; with thin coatings the exposed plate was positive, and with thick coatings negative. This was markedly the case with plates of silver exposed to the vapours of iodine. With vapour of bromine the exposed silver plate was negative, the initial current, even with diffused light, was very strong, but after remaining exposed to light for some minutes then protected from light and again exposed to its influence, it was found that the current was very weak. A film of silver chloride prepared by exposing a silver plate to the vapour of chlorine gave only a very weak effect, but plates coated with the violet subchloride behaved very well in these trials and yielded for a long time results from which comparisons could be made.

On the basis of these experiments Becquerel invented his electrochemical actinometer which was practically a voltaic element or cell composed of two plates of very pure silver coated usually with the violet subchloride of silver and plunged into a conducting fluid composed of two parts of monohydrated sulphuric acid in 100 parts of water. The apparatus was so arranged that all light was excluded, except from an adjustable opening on one side by which one of the plates could be exposed to light while the other remained in darkness.

When diffused daylight or sunshine acted upon one of the plates, more or less deviation of the needle was observed which remained constant so long as the light remained of the same intensity and the surface was sufficiently sensitive. If the light was shut off, the needle returned to zero or somewhat beyond it, but soon regained its original position. If the light remained of the same intensity and the plate was again exposed, the electrical effect was the same as before, always provided that the sensibility of the plate remained the same, for which purpose the sensitive coating should be sufficiently thick. Under favourable conditions the sensibility of the instrument might be preserved for a whole day and thus several consecutive observations might be made.

The deflections of the needle could not, however, be considered as

proportional to the intensity of the chemical action exerted on the substance and consequently to the active luminous intensity; they only shewed whether this luminous intensity was greater or less in one circumstance or in another.

With this instrument Becquerel observed the effect of different rays of the spectrum on silver iodide and violet subchloride, and found that in both cases the maximum of action was in the green about  $D \frac{2}{3} E$ ; but while with the chloride the action decreased on both sides of this point, and ceased at A and H, with the iodide that had already been exposed there was a second maximum in the indigo blue about  $G \frac{2}{3} H$ , and thence the action decreased to P in the ultra-violet. In neither case was any reversed action observed in the red rays, as observed with sensitive papers, but that might be due to the fact that in one case the sensitive surface was in water and in the other in air. Becquerel has not recorded any corresponding observations with silver bromide.

About 1840, Robert Hunt repeated Becquerel's experiments with many modifications, and the results he obtained (*Phil. Mag.*, XVI, 1840), completely confirmed them. More careful trials with the spectrum on plates of different metals made later showed that every ray of the spectrum produces an electrical disturbance. The rays, however, at the least refrangible end, produce a deflection of the needle in one direction, whilst the most refrangible rays set up a disturbance in an opposite direction. There are many indications of a condition analogous to polarity in the action of the prismatic rays. (*Researches on Light*, p. 295.) Hunt also remarks that "This action is only to be regarded as one of the evidences of chemical disturbance, exciting electrical currents; yet at the same time, it opens the question of the identity of the agent producing this disturbance and electricity."

In 1858, Grove (*Phil. Mag.*, XVI., (4), p. 426.) recorded that he had succeeded in obtaining a deflection of the galvanometer needle by allowing a beam of light suddenly to impinge on a daguerreotype plate in a trough of water, the plate being connected with one pole of the galvanometer and a gridiron of silver wire in front of the plate with the other. In experiments with platinum plates he came to the conclusion that the action of light was always in the direction of the polarisation current, though further experiments by Becquerel and others have shown that this is not the case.

In 1863, Pacinotti found that when pairs of plates of copper, zinc, iron or lead were immersed in solutions of certain salts of the same metals, the exposed plate was always negative, but with plates of silver immersed in a solution of nitrate of silver the plate exposed to sunshine

was positive, whereas if exposed to the rays of a petroleum lamp, or of a heated thick iron plate it was negative, as were also the other metals. (*Cimento*, XVIII, p. 363.)

In 1875, Hankel published a series of observations on this subject (*Wied. Ann.*, I, 1877) in which he showed that the electrical behaviour of the metals under the influence of light depended very much on the condition of their surfaces; consequently, in such observations it is necessary to consider separately each state of surface. His observations were made on copper in different states, tin, brass, zinc, platinum and silver. With regard to the latter, he records that when two plates of fairly pure silver were immersed in filtered tap water, the plate exposed to the light of white clouds was negative. When the plates had been left a day in the water the rays of the setting sun still gave a pretty strong negative impulsion. Platinum plates coated with silver were slightly positive with white or blue light, while red light produced no effect. Silver plates coated with platinum, (old platinised silver battery plates) which were slightly negative when coupled in circuit with plain platinum, were found to be very sensitive to light, and the exposed plate was positive. With coloured glasses the action was strongest under blue glass, but was also quite strong under yellow and red glasses; gaslight also produced a pretty strong deviations of the galvanometer needle, and it was found that the action under dark red and blue glasses was stronger than under a light green which was much more transparent.

In 1878, Professor Dewar published a preliminary note on "Experiments in electric photometry," (*Proc. Roy. Soc.*, XXVII, 1878, p. 364) in which he dealt principally with the construction of the best form of cell for the general investigation of the electrical actions induced by light on fluid substances. He found that the list of substances that may be proved to undergo chemical decomposition by light, was very extensive, some of the most active being the ferro- and ferri-cyanides of potassium and the nitroprusside of sodium, tartrate of uranium and a mixture of selenious and sulphurous acids in presence of hydrochloric acid. The complete paper does not appear to have been published.

In 1876, M. Egoroff published a note (*Comptes Rendus, Acad. Franc.*, LXXXII, 1876) on a differential electro-actinometer for the purpose of determining the absorption of the ultra-violet rays by different media. The instrument consisted of two of Becquerel's electro-actinometers placed one above the other and arranged so that the current of one might be neutralised by the other. In some preliminary observations with iodised silver plates he found that the intensity of the current was proportional to the width of the opening through which

light was admitted. It was also inversely proportional to the square of the distance of the source of light from the apparatus. An oil lamp was used. The instrument appeared to show an exact proportionality between the intensity of the light and that of the current, and its great sensitiveness and precision would enable it to be used as a very delicate photometer. In these experiments he found that the electromotive force exerted by the November sun upon iodised silver plates through an opening 30 mm. wide was  $\frac{1}{15}$  of a Daniell cell; with a petroleum lamp, at 8 inches distance, it was only 0.004 Daniell.

Dr. J. Moser afterwards, in 1887, in working on Egoroff's plan found that the photo-electric current might be greatly increased by treating the chlorised, iodised or bromised silver plates with solutions of erythrosin, benzo-purpurin and other dyes, and in sunlight he observed currents of a strength equal to half a volt (Eder's *Jahrbuch der Photographie, &c.*, 1888, p. 297.)

At the meeting of the British Association, in 1880, Professor G. M. Minchin gave an account of his experiments on the generation of electric currents by the action of light on silver plates which were coated with emulsions of bromide, chloride, iodide and other salts of silver in gelatine and collodion, as well as with eosine, fluorescine and various aniline dyes, the object of these experiments being the solution of the problem of producing a photographic image of an object at a distance. A detailed account of these and other interesting experiments on light-cells was read before the Physical Society, and published in the *Philosophical Magazine*, for March 1891.

He found that when two pieces of clean silver foil attached to glass plates were coated with an emulsion of chloride of silver in collodion and immersed in distilled water containing a few grains of common salt, the plates being connected with the terminals of a Thomson's galvanometer and one of them screened from the light, that on exposing the unscreened plate there was an electric current produced, and the exposed plate was *negative* to the unexposed. The same effect was observed with plates coated with emulsions of silver bromide in water containing a little potassium bromide. When the plates were coated with iodide of silver in collodion by the wet silver-bath method, the liquid being water containing a little potassium iodide, there was a reversal of the nature of the exposed plate, it being *positive* to the unexposed. With coloured glasses in front of the exposed plates it was found that the red rays produced comparatively feeble currents, while those produced in the blue and violet rays were very great, but the directions of the current were the same for all rays. This agrees with Becquerel's observations. With plates coated with

an emulsion of silver sulphide in potassic sulphate, the exposed plate was *positive*, the direction of the currents being the same for all rays, the strength of the current being least for the rays passing through the green glass.

With plates coated with an emulsion of silver nitrate in gelatine in a weak solution of barium nitrate, the exposed plate was *positive*. The effect of the red rays was very small, and of the blue rays very great.

One of the most important points in Professor Minchin's observations is his discovery of the formation of an invisible developable deposit on silver plates coated with an emulsion of silver bromide, by the action of the electrical current from a single bichromate cell passing through the plates when immersed in water containing a little potassium bromide. He found (1) that the plate connected with the carbon pole, the cathode, was without the employment of any developer visibly blackened in its immersed part, (2) that no visible change took place on the other plate attached to the zinc, but when the plate was developed with an ordinary pyrogallic acid developer its immersed portion was also blackened. These effects were entirely due to the passage of the current and were strictly confined to those portions of the sensitive plate through which the current passed.

The special bearing of these observations upon the formation and composition of the invisible or visible developable photographic image formed by the action of light, does not appear to have been generally recognised. I began last year a series of observations on this subject which quite confirmed Professor Minchin's: unfortunately they were interrupted before completion, but I hope to resume them in due course, after the completion of the present series, and bring them before the Society on a future occasion.

Professor Minchin also found that by coating silver plates with eosine and gelatine, comparatively strong currents were obtained and the plates were very sensitive to variations in the light. The current generated by daylight in one of these eosine cells was sufficiently strong to produce the photographic action on a silver bromide plate without any preliminary exposure of the bromide plate to gaslight. He also describes a curious case of inversion of the current occurring in the eosine and other cells, which I have also noticed, the initial current being such as to make the exposed plate *positive* to the other. This current, however, was of very short duration and was succeeded by a steady and much stronger normal current in the opposite direction, the exposed plate being *negative* to the unexposed. On suddenly shutting off the light from the plate the instantaneous effect was to

increase the existing current, the effect being merely impulsive, after which the current generally disappeared. This cell having been kept in the dark for a fortnight, it was found that while the inverse currents were produced as before, the initial current on exposure was enormously increased in magnitude and duration. It then disappeared gradually and was succeeded by a current in the reverse direction. When one of these plates was removed from the cell and immersed in water in presence of a clean silver plate, it was at once on exposure to light *negative*, like a silver plate coated in the ordinary way with an emulsion of eosine. In preparing these eosine-gelatine films, it was found to be an advantage to immerse them for a few minutes in a strong solution of alum in order to prevent the dye from washing out of the film too readily.

With silver plates coated with naphthalene red and gelatine the effects were not so strong as with eosine; the exposed plate was *positive* and with strong red rays there appeared to be a reversal of the sign of the E. M. F.

Plates coated with iodine green and exposed to sunshine gave currents with an E. M. F. amounting to about  $\frac{1}{20}$  volt.

M. F. Griveaux, experimenting on silver plates coated with a film of silver iodide, plunged into solutions of iodine of different strengths, circulating through the cell, found that the maximum value of the E. M. F. developed by light acting on one of the plates decreased as the strength of the iodine solution increased, till a certain point was reached at and above which the E. M. F. was *nil*. Also that this point was regulated by the distance of the plates from the source of light; the nearer the plates the higher the concentration point of the solution and *vice versa*. The same effects were observed with silver chloride and bromide. (*Comptes Rendus Acad. Franc.*, CVII, 1888, p. 837.)

I have entered somewhat fully into these previous experiments because very little appears to be generally known about the subject and it seemed desirable to bring together the scattered observations.

In carrying out my experiments I have used two kinds of cells, one horizontal and one vertical, more usually the latter. It consists of a glass cell in which the plates can be coupled face to face or back to back, one being screened from light by the other and by one or two interposed screens of ruby or yellow glass, the cell being covered all round except at an opening on one side. This glass cell is enclosed in a wooden box with a shutter on one side sliding in front of an opening about 1.5"  $\times$  .5", corresponding to the one in the glass cell. In front of this shutter there are grooves in which coloured glasses can

be placed in front of the opening. The upper part of the wooden case is open, but can be closed by a lid, through which, if necessary, a funnel may be passed to admit of solutions being poured into the cell without letting in light. The silver plates used with this cell are 4 inches long, and  $1\frac{1}{4}$  inches wide, other plates, such as photographic sensitive dry plates or celluloid films, being about the same size or smaller.

The other cell is a modification of the form used by Becquerel in his earlier experiments, and consists of a wooden trough divided into two compartments by a double wooden screen which allows the free circulation of the electrolytic fluid, while completely shutting off light from the unexposed compartment. This trough is covered with a lid, having two large openings fitted with hinged shutters, to the underside of which mirrors are attached for the purpose of reflecting light at will on to one or other of the sensitive surfaces in the compartments below. By this arrangement the whole of the sensitive plate can be exposed to light, instead of only part of it, as in the vertical cell, and at the same time the perfect protection of the unexposed plate from strong light is better secured than it is in the vertical cell. This horizontal trough is constructed to take two plates  $3\frac{1}{4}'' \times 4\frac{1}{4}''$  or smaller.

In most cases, even under favourable conditions, the light-currents observed, are exceedingly weak, and therefore a very sensitive form of galvanometer is necessary. The one I have used is the latest modification of the Rosenthal micro-galvanometer made by Edelmann, in Munich. It is said to be the most sensitive form of galvanometer made, enabling currents of about a billionth of an ampère to be read with a resistance in the coils of only 1,000 ohms. It is fitted with a telescope by which direct readings are made off the mirror from a millimetre scale placed at one metre from it. In this position and without the directing magnet, using the  $\frac{1}{10000}$  shunt, with a total external resistance of about 60,000 ohms in circuit, the deflection caused by one gravity-Daniell cell is one millimetre division of the scale. By using the directing magnet the normal sensitiveness of the instrument can be very greatly increased, though in most of the experiments it has been found sufficiently sensitive without the magnet, and when used, the increase of sensitiveness has been limited to about five times the normal. The instrument can be set up in any position, is simple in construction and I find it very sensitive, convenient in use and easy to observe with fair precision, considering the difficulty there is in obtaining freedom from shake and tremor in a city like Calcutta built on a bad foundation of mud. In reading the scale which is 50 centimetres long,

sub-divided into millimetres, I have usually fixed the zero point at 30, so that the readings above or below it may as far as possible show different signs of E. M. F., and the direction of the currents has been so arranged that a change in the position of the index to the apparent left from 30 to 0 shall indicate that the exposed plate is *negative* to the unexposed, as copper to zinc, while a change to the apparent right, 30 to 50, shows that it is *positive*, or as zinc to copper.

The coloured glasses used have been of the kinds ordinarily met with in the bazar. A deep ruby, a brownish yellow, a medium green, and a dark blue, and conditions being favourable it has generally been possible to observe some trace of a current even with the deep ruby in strong sunshine.

When observations were made with the spectroscope, whether with a Rowland's diffraction grating or prisms, it was found that the amount of light admitted through the slit for ordinary work, was quite inadequate, even when the slit was open at its widest; and it was therefore necessary, in most cases, to use a much wider slit, or to dispense with its use altogether; also to use the directing magnet on the galvanometer to increase the sensitiveness.

In all cases sunshine has been reflected on to the sensitive plates by means of a heliostat, as it was not convenient to use the direct rays of the sun. With the flat cell there were thus two reflections, but any loss of light was amply made up by the increased surface exposed.

As is usual in such experiments, there were almost invariably more or less strong local or polarisation currents generated between the plates themselves, especially when they were freshly immersed in the solutions, and it was generally found desirable to leave the cell from 12 to 24 hours before use, so as to give time for these currents to subside. Sometimes, however, from half an hour to an hour, or even in some cases a few minutes is sufficient. It was found, too, that even if there was no polarisation current at the commencement of an experiment, the action of light occasionally gave rise to fairly strong currents quite independent of, and sometimes opposed to, the currents produced by exposure to sunshine, while at others they were in the same direction. Thus it was sometimes difficult to ascertain how far the currents observed were due to light or to polarisation. The only test was the retrograde movement of the needle after shutting off the light.

Another difficulty in making these observations may be noted, and that is, the apparent reversals of current which are due in many cases to decrease in the strength of the light, though the decrease may be almost imperceptible. For the same reason, if coloured glasses be applied without first completely shutting off the light after the plates

have been exposed to sunshine, there is an apparent reversal due to the loss of power in the light, and not to change of direction of the E. M. F. As a rule my observations with coloured glasses or the spectrum have agreed with Becquerel's and Minchin's that no reversal of sign is produced by any of the coloured rays. At the same time, I have found that in some cases the blue rays appear to have a reversing tendency, as might be anticipated from their very strong reversing action on certain forms of sensitive photographic plates containing iodide or bromo-iodide of silver. This point, however, requires much more complete investigation with the aid of the spectroscope, and will be further considered when dealing with the silver haloids. During the time I have been engaged with these observations, the weather has been unusually changeable and cloudy for the time of year, and hence it has been difficult to compare the results of observations on different days. For this reason it has been impossible to give more than general indications of the amount of deflection caused by the action of light in the cases recorded: exact observations would have to be made with a standard light.

It seemed desirable to commence the observations with experiments on plain silver plates in different fluids. The plates used were not quite pure, having been reduced from various silver residues, and were about .974 touch. They were four inches long and one and a quarter inch wide, and were usually cleaned with fine emery powder, or with emery cloth immediately before and after use. It is, however, better to make sure of the purity and cleanliness of the surface of the plates for each operation by heating them red-hot and then immersing them in dilute sulphuric acid. As facilities for doing this with thick plates were not readily available, it has been omitted in all the following observations. As a rule, the plates were immersed in the solutions to a depth of from 2 to  $2\frac{1}{2}$  inches, care being taken to avoid moistening the upper unimmersed parts by capillary action or otherwise, and so exposing them to irregular currents from this cause. The plates were about half an inch apart, being kept separated by two wooden blocks with a dark ruby glass plate between them.

## I. SILVER PLATES IN WATER.

### *Distilled Water.*

Distilled water being almost a nonconductor, the currents observed were naturally exceedingly weak and could only be clearly seen with strong sunshine. The deflection observed without the magnet varied from .5 to 3 divisions of the scale, and in nearly all cases the exposed plate was positive to the unexposed, and formed the anode or dissolving plate of the couple. In some cases the exposed plate became more

sensitive after the first exposure, but after a few exposures lost all sensitiveness. The current being so small, it was not thought necessary to experiment with coloured glass or the spectrum. With the directing magnet placed as before described the deflection was increased to about 6·5 divisions.

#### *Tap Water.*

The tap water used was the filtered Hooghly water, supplied in the town mains. It is fairly pure and free from lime salts, but chlorides are present in moderately large proportion, the amount of chlorine varying from ·5 to 1·4 parts per 100,000, and at the time of the experiments it would be about 1 to 1·2 parts per 100,000. The total hardness varies from 3·15 to 11·5 parts and would be about 9 parts per 100,000 at the time of the experiments. In most of the cases observed the exposed plate was distinctly positive to the unexposed, as with distilled water; but in some cases it was negative, and in one or two instances the action was irregular. The plates were rather more sensitive than they were in distilled water, the normal deflections without the directing magnet varying from 1 to 7 divisions of the scale, but usually they were between 2 and 4.

In one case in which the plates had been in the cell for about 38 hours, and there was only a very slight cell-current, exposure to sunshine gave a deflection of + 4·5 divisions without the magnet, but with it the deflection in bright sunshine rose to + 20 divisions, and even in diffused light was + 5 divisions. Exposing under ruby glass gave a deflection of + ·5; yellow glass + ·7; green glass + 1; blue glass + ·5 in diffused light, and + 7·5 in sunshine. Trials were also made with the grating spectroscope without the directing magnet, but the results were not conclusive and the unsettled weather has, so far, prevented their being repeated with the galvanometer in its most sensitive state. The plates were found very sensitive to changes in the strength of the light, but after repeated exposure to sunshine they seemed to lose sensitiveness. By the action of the water a greyish deposit of chloride was formed and in some cases a darkened image of the exposed part of the plate could be seen. It may be noted that my experience does not agree generally with that of Hankel, who found that, of two silver plates immersed in water the plate exposed to white clouds, or to the setting sun, was negative. I find, however, that on one occasion when fresh plates were exposed to daylight, the exposed plate was negative, the deflection being about - 1·5 divisions of the scale. On again exposing the same plates to sunshine the exposed plate was positive, and remained so afterwards on further exposure. On two other occasions of expo-

sure to daylight, the exposed plate was also negative. When exposed to sunshine the plates were almost invariably positive. I have noticed this difference with plates in other solutions.

## II. SILVER PLATES IN DILUTE ACIDS.

As we have seen above, Becquerel found that with plates of gold or platinum, immersed in acid solutions, the plate exposed to the light was always positive. The same rule seems to apply to silver plates in most cases, but not in all.

### *Dilute Sulphuric Acid.*

The action of dilute sulphuric acid upon silver plates under the influence of light seems to be rather irregular, but I find on looking through all the experiments made, that in nearly all cases the first exposed plate of each pair had a negative tendency when first exposed, though it might become positive by subsequent exposures and in the same way the second plate of the pair, which was screened during the first exposure, might also be positive on first exposure. The general tendency was undoubtedly positive. The irregularities may be partly due to the plates not being quite pure.

With silver plates immersed in distilled water acidified with about a drop of acid in some 60 cc. of water, the exposed plate was generally positive when exposed to bright sunlight, the deflection without the directing magnet varying from 1 to 4.5 divisions of the scale, sometimes increasing after repeated exposures. In one experiment, however, the exposed plate was distinctly and uniformly negative, even after the position of the plates had been reversed, but subsequent exposure of the reversed plate made it positive. In another it was negative on first exposure and then positive.

With a pair of plates in tap water, acidified in the same way, the plate exposed to sunshine was first negative with a deflection of -3 divisions on the scale, which increased to -6 divisions by subsequent exposures. Exposure under coloured glasses also gave a negative deflection, amounting with red glass to -1, with yellow and green glasses to -2; with blue glass to -5, and exposed to sunshine again -6, as before. The same plates being again exposed to sunshine later on were also negative at first, but became positive and much more sensitive. Under coloured glasses the deflections were also positive and very much larger than on the first exposure of the plate. After reversal, so that the former unexposed plate became the exposed plate, the deflection was again negative, amounting to -7 divisions, and increasing with the exposure. These plates were very sensitive to changes in

light, and there was a perceptible deposit of chloride (?) on their immersed surfaces.

With plates immersed in a 1 per cent. solution of sulphuric acid in distilled water, it was found that if the plates were exposed to sunshine a very short time after being immersed in the dilute acid, they were at first negative and fairly sensitive to light but afterwards became positive; whereas in a case when the plates were left standing for 24 hours to reduce the polarisation, they were positive, and much less sensitive than the plates which were negative. After a short time they seemed to lose all sensitiveness.

In tap water containing the same proportion of acid, the exposed plates were generally positive on opening the shutter; but the current quickly decreased, and with some plates after several exposures they gave a negative deflection.

With plates immersed in distilled water containing two per cent. of acid the deflections were usually positive and the plates seemed to become less sensitive by repeated exposure and by keeping.

With plates immersed in dilute acid at 5 per cent., which had been allowed to stand for 24 hours, and showed a very small cell-current, the first plate of the pair was distinctly negative when exposed, the deflection being  $-4$ , decreasing with exposure to  $-2$ , but the second plate when exposed after reversal of the plates in the cell was positive with a deflection of  $+6$ . Two other pairs of plates in freshly-mixed acid were positive on first and subsequent exposures. The addition of acid lowered the sensitiveness of the plates considerably.

All the plates showed a slight grey deposit or stain on the immersed ends, but no trace of an image.

#### *Dilute Nitric Acid.*

With nitric acid the exposed plates are nearly always positive and the action is far more uniform than with sulphuric acid, especially when an appreciable quantity of acid, as one per cent. and over, is used. Becquerel also found the exposed silver plate positive in dilute nitric acid.

With distilled water acidified with about 1 drop of acid in 70 cc., the exposed plate was positive on first exposure, but afterwards became negative. The plates were not very sensitive, the deflections without the directing magnet varying from 1 to 3 divisions of the scale.

With 1 per cent. of nitric acid, *sp. g.* 1.250, in distilled water, after 14 hours standing, the exposed plate was uniformly positive, and more sensitive than with the acidulated water, the deflections in sunshine being from 3.5 to 5.5 divisions, without the directing magnet. There

was a slight greyish deposit on the plates, but no image on the exposed part.

With three per cent. of the same acid in distilled water, after 22 hours standing, the first plate exposed in weak sunshine first showed a negative deflection of 2 divisions, and after that was positive, the deflection of repeated exposures being steadily about + 5 divisions, without the magnet. With the directing magnet, the deflection was about + 20 divisions with the 100 ohm, or  $\frac{1}{10}$ , shunt.

After the experiment the solution was found to contain silver.

#### *Dilute Phosphoric Acid.*

With dilute phosphoric acid the deflections were almost always positive. Plates freshly immersed in a mixture containing 1 per cent. of the acid, sp.g. 1.750, in distilled water and exposed to sunshine, gave an initial deflection, without the magnet, of + 23 divisions, but this quickly decreased with further exposure. After shutting off the light the cell-current was found to have increased, and on again opening to sunshine the deflection seemed slightly negative, but the action generally was irregular. Subsequent exposures with the same cells or after the plates had been reversed showed positive deflection and the plates were less sensitive than at first.

With the same acid at 5 per cent. the deflections were uniformly positive. With plates exposed to sunshine after 16 hours, the deflection without the magnet was + 8 divisions, but, as in the former case, it was less on subsequent exposure. The same decrease of sensitiveness after exposure was noticed with the plates after reversal in the cell.

#### *Dilute Hydrochloric Acid.*

With 1 per cent. of hydrochloric acid, sp. g. 1.150, in distilled water, the exposed plates have shewn themselves uniformly positive, and owing to the formation of a deposit of chloride they are much more sensitive to light, than are plates immersed in acids which do not form a sensitive compound with the silver. The deflections with sunshine, without the directing magnet, were from + 6 or + 7, when the plates were first exposed, to + 36, when they had been kept for some hours longer and then exposed. The plates were covered with a greyish deposit of chloride on the immersed parts, and there was a distinct darkened image on the part of the plate exposed to light. Coloured glasses all gave positive deflections, the red being the smallest, and then the green.

With 3 per cent. acid, after 22 hours resting, the plates exposed to sunshine were positive. The increase of acid seemed to reduce the sen-

sitiveness very much, the highest deflection in sunshine, without the directing magnet, being + 16, while after the plates had stood for 37 hours it was only + 11.

There was a dark grey deposit of chloride on the immersed parts of the plates, which took a violet or purple colour on exposure to light, and gave off an odour of chlorine.

#### *Dilute Hydrobromic Acid.*

With dilute hydrobromic acid containing 10 cc. of the ordinary pharmaceutical dilute acid, of 10 per cent., to 100 cc. distilled water, the plate exposed to sunshine or diffused daylight was uniformly *negative* and extremely sensitive to light, the first deflection in bright sunshine being about - 187 divisions, without the directing magnet, decreasing to a steady reading of about 140 divisions. Even coloured glasses gave fairly large deflections; red, - 13; yellow, - 54; green, - 64; blue, - 103.

With dilute acid of double the above strength, the exposed plate was also uniformly negative, but the plates did not seem so sensitive, the deflection in sunshine, without the magnet, being only - 82; but the readings depend very much on the strength of the light, and this was variable at the time of observing.

In both these cases the plates were coated with a grey-greenish-yellow deposit of bromide, which turned dark on exposure, and formed a visible image of the exposed part of the plate.

#### *Dilute Hydriodic Acid.*

As pure hydriodic acid is somewhat troublesome to prepare, I roughly made up a solution of it by precipitating one gramme of barium iodide, dissolved in water, with sulphuric acid and adding water to make up 100 c.c. There was, however, a considerable quantity of free iodine present, the solution being of a light sherry colour.

The cell containing two clean silver plates immersed in this solution was left standing for 15 hours. The plate exposed to sunshine was then found strongly negative, the deflection, without the directing magnet, being - 110 divisions of the scale, afterwards going up to - 130 divisions. The plate was, very insensitive to weak daylight, the reading being only 12 divisions when the sun was hidden behind clouds. With coloured glasses fairly large deflections were obtained, always in the same negative direction; red glass giving - 15 with daylight, and - 16 with sunlight; yellow - 16.5 with daylight, and - 20 with sun; green - 14 with daylight, and - 19 with sun; blue - 16 with daylight, and - 80 with sun. By keeping, the plates

became less sensitive. They were covered with a strong loose deposit of iodide, under which the silver surface was darkened. A faint image of the exposed part was visible.

*Dilute Glacial Acetic Acid.*

With plates freshly immersed in dilute glacial acetic acid of 1 per cent., the plate exposed to sunshine was positive, the deflection being about + 6.5 divisions, without the magnet; a second exposure gave a deflection of + 8.3 divisions. By keeping for 24 hours the plates were less sensitive, but remained positive.

Plates immersed in dilute acid of 5 per cent. and kept 24 hours before exposure were less sensitive than the above, the deflection with sunshine being only + 3 divisions without the magnet, and they became less sensitive by further exposure, but were always positive.

*Dilute Formic Acid.*

The only other organic acid I have yet tried is formic acid, one per cent. in distilled water. After the cell had been standing 24 hours, exposure to sunshine gave a deflection amounting to about 8 divisions, the exposed plate being positive. The same plates after another 24 hours standing were found to have become very insensitive, the deflection being only one or two divisions of the scale, the exposed plate still being positive.

### III. SILVER PLATES IN ALKALINE SOLUTIONS.

Becquerel found that when platinum or gold plates were immersed in alkaline solutions, the plate exposed to light was negative. So far as my experience goes, this rule does not hold good with silver, the sign of the exposed plate being almost always positive. I have not tried these solutions very thoroughly, but the results obtained with potash and other salts used seem conclusive.

*Solution of Potassium Hydroxide.*

With a solution of one per cent. of caustic potash in distilled water, the cell having been standing 22 hours, the cell current was *nil*.

Exposure to bright sunshine gave a deflection of about 9.5 divisions without the magnet, the exposed plate being positive. With the magnet the deflection was about + 45 divisions in sunshine, and + 9 divisions in daylight. With sunshine under blue glass the deflection, with the magnet, was + 31; under green + 9; yellow + 8; red + 4.5. There was no deposit on the plates and no image of the exposed parts.

*Solution of Potassium Carbonate.*

With a solution of one per cent. of anhydrous potassium carbonate, the cell having been standing for about 14 or 15 hours, the cell-current was very small, and the plate exposed to light, either daylight or sunshine, was found to be positive, the deflection in the former case being + 22, and in the latter + 63·5, without the magnet.

With tap water made alkaline with a few drops of ten per cent. solution of the carbonate in about 60 c. c. of water, the exposed plates were also positive and very sensitive on first exposure, but the current decreased with further action of light, and in subsequent exposures the plates were less sensitive to light. They also lost sensitiveness by being kept in the cell.

*Solutions of Sodium Carbonate.*

With silver plates exposed shortly after immersion in 1 per cent. solution of anhydrous sodium carbonate in distilled water, the plate exposed to sunshine was positive, the deflection being about + 5 divisions without the magnet. In subsequent exposures the plates were less sensitive, but remained positive.

With a stronger solution, at 5 per cent., the results were similar, but the plates seemed somewhat more sensitive.

*Solution of Lithium Carbonate.*

With plates exposed shortly after immersion in a 1 per cent. solution of lithium carbonate in distilled water, the plate exposed to sunshine was positive, the deflection being about + 6 divisions without the magnet. The plates lost sensitiveness after the first exposure as well as by keeping for 34 hours, but remained positive.

*Dilute Solution of Ammonia.*

With a solution of 4 c. c. of strong liquid ammonia in 100 c. c. distilled water, the cell having been left standing some 14 or 15 hours, the plates were found to be exceedingly insensitive to light; even with the magnet the deflections in sunshine were only about 2 divisions, the exposed plates being positive.

Another pair of plates immersed in a freshly-mixed solution, containing 2 c. c. of liquid ammonia in 100 c. c. of water, and exposed soon after immersion, were also found insensitive, but not so much so as the last; the deflection on first exposure in sunshine being about 3 divisions, without the magnet. The current, however, decreased on further exposure, and the same effect was observed in subsequent exposures. After a short time no current was perceptible.

The immersed parts of the plates showed no deposit.

*Potassium Cyanide.*

With a solution of potassium cyanide in distilled water, about 1 per cent., there was a strong negative polarisation current in the cell when first prepared, which took several hours to subside. When freshly immersed the exposed plate was negative, but not very sensitive, the deflection without the magnet being only  $-4$  divisions for sunlight. By keeping the cell 24 hours the polarisation current subsided entirely, and the plate exposed to sunshine was again negative with a deflection of  $-3.5$  divisions. A slight movement of the cell, however, seemed to cause a reversal of the current with a deflection of  $+6.5$  divisions which further continued for another  $6.5$  divisions after the light had been shut off. The same effect was observed on subsequent exposures, first the plate was negative then positive, while the polarisation current increased in the same direction. After a time the plate seemed to become quite insensitive to light.

With the same plates reversed there was again a very large initial negative polarisation current. On first exposure of a plate to sunshine the deflection was  $-14.4$  divisions, without the magnet. On shutting off the light, the negative polarisation current was found to have very largely increased. On second exposure the plate was first negative and then positive. On shutting off the light the current continued  $+2.5$  divisions in the same direction and then turned back in its original direction. The plates were coated with a dark grey deposit, thicker at the upper part of the plates than at the lower. About the immersion line there was a yellowish-white deposit, and the plates were deeply corroded, but no sign of an image of the exposed part was visible.

From the above experiments it would appear that as a general rule sunlight has an oxidising or dissolving effect on silver, whether in acid or alkaline solutions, the exposed plates being nearly always positive and consequently forming the anode of the voltaic couple. With solutions decomposed by silver and forming sensitive compounds the action is variable.

## IV. PLAIN SILVER PLATES DRY.

When a comparatively large silver plate about  $5 \times 4$  inches, not immersed in any solution, but with its ends connected by silver bands to the terminals of the galvanometer, the directing magnet being specially placed so as to increase the normal sensitiveness about 13 times, was exposed to light so that the upper half remained unexposed, it was found possible to detect a slight current between the exposed and unexposed halves of the plate; the exposed half being positive to the unexposed. With an uncleaned plate that had lain in a drawer for

some months, the deflection in sunshine was fairly large, amounting to about 10 divisions, or rather more than the deflection caused by the contact of dry zinc and copper. When, however, the same plate had been carefully cleaned with a solution of cyanide of potassium followed by the usual rubbing with emery cloth, the deflection was found to be still positive, but much smaller, being only about 1·5 divisions on first exposure, and by repeated exposure it was reduced to about ·25 division.

With subsequent exposures the deflection was generally in the same direction, but once, after fresh cleaning, it was negative. With a plate of pure silver deposited on glass, freshly polished, the first exposure gave after a short interval, a fairly strong negative deflection, but with subsequent exposures at intervals the deflections have been sometimes negative and sometimes positive, but always very small, so that the observations are somewhat uncertain. Plates of almost perfectly pure silver, 999·5 touch, obtained through the kindness of the Mint Master, Lt. Col. Baird, R. E., F. R. S., gave also rather indefinite results, owing to the smallness of the currents, and though the deflections were generally positive on first exposure of the plates, they were sometimes negative, or became so by prolonged exposure. The general tendency, however, appeared for the plates to be positive under the influence of light, and, if this is the case it would seem to point to some slight oxidising action on the surface. At the same time, the results obtained with *pure* silver and the fact that in so many cases the deflections have been first positive and then negative, appear to favour the conclusion that such plates are really negative. It was clearly ascertained that the currents produced were not due to the action of heat, because with the plate first observed and with the purest silver plates, the action of heat applied at the exposed end of the plate was to give a positive deflection, but with the less pure silver plates used in the cells and others largely alloyed with copper, the heated end of the plate was always negative to the cool end. The deflection invariably increased with the continuance of the heating, and was always in the same direction on repetition of it.

The light currents, on the other hand, showed a decrease of deflection from repeated exposures and sometimes a change of sign in a direction contrary to the heat currents shown by the same plates. The observation is rather a difficult one and requires further repetition under more favourable conditions of light, in order to obtain definite results.

I have also tried the effect of solutions of alkaline haloid salts upon silver plates, but as this paper is already beyond the usual limits, it may be well to defer the account of these and other experiments on photographic plates containing the haloid salts of silver to a future paper.

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